

ALTERATION OF THE FREE SURFACE ENERGY OF
SOLIDS. I

VERTICAL-ROD METHOD FOR THE MEASUREMENT OF
CONTACT ANGLES AND PRELIMINARY STUDY OF
EFFECT OF HEAT TREATMENT ON MAGNI-
TITUDE OF CONTACT ANGLES

BY
JULIAN L. CULBERTSON

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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VERTICAL-ROD METHOD FOR THE MEASUREMENT OF CONTACT ANGLES AND PRELIMINARY STUDY OF EFFECT OF HEAT TREATMENT ON MAGNITUDE OF CONTACT ANGLES

The angle of contact formed between solid, liquid, and gas, or between solid, liquid, and liquid is a function of the tensions existing between the phases in contact. Since the surface tension of a phase is numerically equal to its free surface energy, measurement of contact angles is of importance in connection with studies of free surface energy relations of given systems. Various methods have been employed for measuring the contact angle, as for example, the sessile-drop method, transparent-capillary-tube method, tilting-plate method, rotating-cylinder method, bubble method, drop-on-horizontal-plate method, combination drop-volume and capillary-ascension method, pressure-of-displacement method, and others. Any one of these methods will give reliable results provided it is used under properly controlled conditions. It is of greatest importance that the exact treatment history of the solid phase be known. Failure of different investigators to use solids with the same treatment history accounts largely for the divergent values for contact angles found in the literature.

It became desirable in connection with our researches to adopt some method with which measurements could be carried out rapidly. Preliminary tests indicated that readily duplicable results could be obtained by immersing the solid, in the form of a rod, vertically through a horizontal liquid interface. Other investigators had used a vertical-rod method (4, 7) or a vertical-plate method (2, 3) in investigations dealing with surface energy relations, but no simple rod method had been described which gave readily duplicable results for solid-liquid-air angles and for all types of solid-water-organic liquid interfacial angles. Such a method was developed and has been used throughout this investigation. This method will be referred to as the "vertical-rod" method.

VERTICAL-ROD METHOD FOR OBSERVING SOLID-LIQUID-AIR CONTACT ANGLES

For the measurement of solid-liquid-air contact angles the solid rod was placed vertically through the liquid surface, and a microscope in a horizontal position was focused on the system with the line of contact of the liquid with the solid approximately in the center of the field. In order to secure a true representation of the configuration of the surfaces in such a system, it was necessary that any liquid or solid through which the illuminating light ray was passed be bounded by plane surfaces and be of uniform thickness. For the case of solid-liquid-air systems in which the contact angle was less than 90° it was easy to arrange the apparatus so that observation could be made without having the light ray pass through any liquid or solid media. This was accomplished by filling to the brim with the liquid to be investigated a small rectangular glass cell having one horizontal dimension of approximately 1 cm. (figure 1a). The cell was mounted against the microscope stage and was adjusted so the surface of the liquid appeared in the field of the microscope unobstructed by the sides of the cell. The liquid surface under these circumstances was unprotected

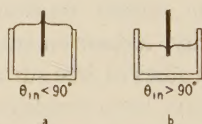


FIG. 1. Cell used for observing solid-liquid-air contact angles

from atmospheric contamination, and it was found best to enclose this small cell in a larger rectangular cell which could be covered except for the small aperture through which the rod was inserted. The large cell had walls of clear plane polished glass.

In case the solid-liquid-air angle, θ_{ln} , was greater than 90° and there was a depressing of the liquid around the rod, the light beam had to pass through the liquid. For this case the cell was but partially filled with the liquid (figure 1b). The illuminating beam of light passed through the cell walls and through the body of the liquid. Since the cell walls were plane and were parallel to each other there was no distortion of the image in the microscope.

VERTICAL-ROD METHOD FOR OBSERVING SOLID-LIQUID-LIQUID CONTACT ANGLES

The arrangement of apparatus used for interfacial solid-liquid-liquid systems depended upon the characteristics of the system under investigation. When water and an organic liquid (immiscible with water) were poured into the cell and a rod inserted, a contact angle solid(rod)-water-organic liquid, θ_{ns} , represented in figure 2, a, b, c, or d, was formed. An-

other contact angle, solid(cell wall)–water–organic liquid, was also formed. Since the cell walls were of glass, they were more readily wetted by water than by organic liquid and the interfacial contact angle of the liquids with the cell wall, when measured through the water phase, was acute. The interfacial angle solid(rod)–water–organic liquid, θ_{n3} , could readily be viewed through a microscope in a horizontal position at the side of the cell in cases a and b, but in cases c and d the interfacial angle solid(cell wall)–water–organic liquid obscured the view. In such cases devices such as are shown in figure 2, c' and d', were utilized. In the diagrams n refers to organic liquid, 3 refers to water, the symbol θ_{n3} represents the solid(rod)–water–organic liquid angle which is expressed as measured through the water phase, and symbols d_n and d_3 represent the densities of organic liquid and water, respectively.

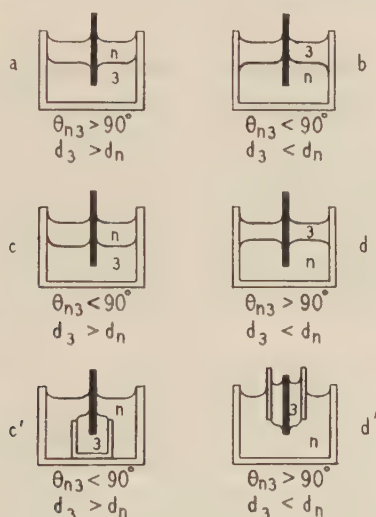


FIG. 2. Cell used for observing solid-liquid-liquid contact angles

Situation c was realized with a silica–water–benzene system. Proper conditions were attained in this case by filling the small (inner) cell to the brim with the denser liquid, and allowing the lighter liquid to flow into the larger cell until the small cell was completely submerged. This gave a liquid–liquid interface at the top of the small cell which was slightly convex upwards. When the rod was thrust vertically through the interface, the angle of contact of the interface on the solid being acute with respect to the denser liquid, the interface rose slightly and was easily brought into the field of the microscope.

Situation d was realized with a silica–water– α -bromonaphthalene system. To obtain an unobstructed view of this system a glass tube, open

at both ends, was supported vertically in the larger cell, with the lower end of the tube at least a centimeter from the bottom of the cell. The lower end of this tube was ground flat, normal to its axis. The tube was about 5 cm. in length and had an inside diameter such that when the solid rod, on which the measurement was to be made, was fixed in its center there was 3 mm. or more of clear space between the rod and the inside wall of the tube. The denser of the two liquids was first run into the cell until the lower end of the open tube was completely submerged. Then by adding the lighter liquid at the top of the open tube, the liquid-liquid interface was pushed down the tube by hydrostatic pressure until it became visible at the lower end of the tube. The solid rod on which measurements were to be made was placed in the center of the tube and was then extended through the liquid-liquid interface. The interfacial contact angle thus formed was easily observed and photographed.

Method of measuring angles

The system to be examined was carefully adjusted; light from an arc was focused upon the rod so as to give good illumination of the line of contact. A microscope in a horizontal position was focused upon the points of contact at the maximum observable diameter of the rod, and photomicrographs were taken. The angles were either measured directly upon the photographic plate (lantern slide size) by means of a specially designed tangent-meter or were measured from the image projected upon a screen.

PRELIMINARY EXPERIMENTS ON EFFECT OF HEAT TREATMENT ON MAGNITUDE OF CONTACT ANGLES

Pyrex and silica rods 1 to 3 mm. in diameter were cleaned by treating with dilute nitric acid, washing with a large quantity of water, steaming, and heating to 450°C. in air for three hours. When these rods were cooled very slowly, they exhibited zero solid-water-air contact angles. When they were cooled rapidly, they gave small finite contact angles with water. Cleaned rods, 3 mm. in diameter, were drawn out to less than 1 mm. by heating either in a blast flame or in a platinum resistance coil. The solid-water-air contact angle varied from a value of zero on the 3-mm. and 1-mm. portions, i.e., maximal and minimal diameters, respectively, to over 30° on the conical section of the rod.¹ Upon examination of the conical section in polarized light, an intense strain was revealed.

Pyrex-organic liquid-air and pyrex-water-organic liquid contact angles were also investigated with such drawn-out rods, but quantitative correla-

¹ A similar observation was made in this laboratory by Bartell and Stenzel who observed finite Pyrex-water-benzene contact angles within cone-shaped capillary tubes (unpublished observation).

tion of the free surface energy changes was impossible because of the impossibility of exactly duplicating a stressed specimen.

Freshly fused, rapidly cooled, solid Pyrex spheres of several millimeters diameter also showed an intense strain when examined between crossed Nicols. Such spheres gave an angle of about 80° with water. It has been suggested that tangential surface stresses exist upon rapidly cooled solid glass spheres (8). Removal of the strain by careful annealing caused the spheres to give zero solid-water-air contact angles. It is interesting to note that freshly blown hollow Pyrex bulbs gave zero solid-water-air contact angles; these bulbs appeared unstrained when examined in polarized light.

To substantiate the results with stressed specimens, the drop-on-plate method was employed. Compression of a Pyrex glass plate caused the solid-water-air contact angle to increase from zero to about 10° . Release of the compressive force gave a surface which showed a zero contact angle with water. When brass plates were subjected either to compressive or to extensive stress, the solid-water-air contact angle could be increased from a value of 45° to a value of about 60° .

Carefully annealed glass surfaces, giving zero solid-water-air contact angles, when allowed to stand in air showed an increase of contact angle with time of standing (6). Such changes were generally of the order of 15° to 20° for glass, but even greater effects were obtained with advancing angles on metals. Sorption of gases or vapors (5) from the air may have been responsible for these changes.

EFFECT OF HEAT TREATMENT ON SILICA

The effect of heat treatment on solids seemed, from the preliminary tests, to be readily duplicable in the absence of strain. The major portion of the remainder of this investigation has been concerned, therefore, with such effects under diverse, though exactly defined, conditions.

A summary of results obtained with silica against α -bromonaphthalene and against acetylene tetrabromide is given in table 1.

The results illustrate clearly that the previous treatment of the solid is an important factor in determining the size of the contact angle. A fresh silica surface, that is, one that had been prepared by carefully drawing out a large, clear, fused silica rod, showed a moderate hysteresis effect, or difference between the advancing and receding contact angles with α -bromonaphthalene and acetylene tetrabromide. Silica that had been cleaned with hot chromic acid, washed with water, steamed, and dried at 100°C . showed approximately the same effects.

A silica rod that had been heated to 400°C . gave an advancing angle of practically the same value as the receding angle. This change was not permanent, however, for if the silica that had been heated at 400°C . was

allowed to stand for a few hours in dry air the contact angle returned to a value as great as or greater than the original value for the freshly drawn rod. Contact angles could be readily duplicated to $\pm 4^\circ$. The general results obtained were in good agreement with those presented by Bartell and Wooley (1) for similar systems, but obtained by a different method of measurement.

TABLE 1

Advancing and receding contact angles for the systems α -bromonaphthalene-silica-air and acetylene tetrabromide-silica-air

PRETREATMENT	HEAT TREAT- MENT TEMPER- ATURE	TIME OF HEATING	α -BROMONAPHTHA- LENE		ACETYLENE TETRABROMIDE	
			θ_a^*	$\theta_r^\dagger$	θ_a	θ_r
	$^\circ\text{C.}$	hours				
Newly drawn surface.....			12°	5°	19°	14°
Steamed.....	100	1	13°	6°	21°	16°
Steamed.....	400	1	6°	5°	15°	14°
Steamed.....	400	3	0°	0°	15°	14°
Steamed.....	400	3 $\frac{1}{2}$	15°	6°	22°	15°

* θ_a = advancing contact angle.

† θ_r = receding contact angle.

‡ Then stood in dry air at 25°C. for 12 hours.

EFFECT OF HEAT TREATMENT ON METALS

Gold and platinum were chosen for the study of contact angles on metals. Because of their resistance to corrosion it was believed that surfaces of greater constancy in properties could be obtained with these metals than with less noble metals. When these metals had been heated, both the advancing and receding solid-water-air contact angles were found to have decreased. In order to evaluate if possible the effect of heating upon the behavior of the metal surface, a method of pretreatment of the surface was sought by means of which one might obtain a surface in an easily reproducible condition. The criterion of constancy of surface condition was the solid-water-air contact angle formed on the metal surface.

The surfaces of the metal rods were carefully polished with the edge of a finely ground glass plate, washed briefly in acid, washed thoroughly with water, steamed, and then heated in an oven at 100°C. for one hour. It was found that the surfaces so prepared exhibited with water, within comparatively narrow limits, $\pm 4^\circ$, the advancing and receding angles of contact shown in table 2.

Heating to higher temperatures caused a decrease in both the advancing and receding angles. A fairly wide variation of values was found with some of the systems, which indicated that it was not easy to reproduce, exactly,

surface conditions of the solid. The free surface energies of the solids appeared to change rapidly when exposed to air at room temperature, as was noted by taking contact angle readings at intervals of even a few minutes (6). Metal surfaces differed from silica surfaces in that there was no apparent tendency for receding angles to increase upon exposure of the surface to air for a period of time. It was evident that in a study of metal surfaces great care must be taken to follow given methods of pretreatment so as to prepare standard surfaces for use as surfaces of reference.

TABLE 2
Contact angles of the water-gold and water-platinum systems

TREATMENT	CONTACT ANGLES	
	Gold	Platinum
1. Metal polished, steamed, heated at 100°C. for 1 hour		
Water advancing.....	70°	63°
Water receding.....	40°	28°
2. Metal polished, steamed, heated at 600°C. in air for 1 hour		
Water advancing.....	13°	0°
Water receding.....	0°	0°
3. Metal polished, steamed, heated at 600°C. in hydrogen for 1 hour		
Water advancing.....	20°-30°	35°-41°
Water receding.....	0°	0°
4. Metal polished, steamed, heated at 600°C. in air for 2 hours		
Water advancing.....	0°	0°
Water receding.....	0°	0°
5. Metal polished, steamed, heated at 600°C. in air for 2 hours, then 24 hours in air at 25°C.		
Water advancing.....	65°	
Water receding.....	0°	0°
6. Metal polished, steamed, heated at 600°C. in air for 1 hour, then 24 hours in air at 25°C.		
Water advancing.....	55°	51°
Water receding.....	0°	0°

Measurements of interfacial contact angles formed on metals by the interface water-organic liquid were also made. The values obtained varied within fairly wide limits, depending upon the precise pretreatment of the solid, just as did the values for the solid-water-air angles. Data obtained will not be presented in this paper, inasmuch as results have since been obtained for similar systems, but with metal rods that were pretreated in a manner which has been found to give more exact and reproducible results. These results will be presented in an early paper.

SUMMARY

1. A method has been developed for the measurement of contact and interfacial contact angles against either transparent or opaque solids which can be formed into rods. This method is called the vertical-rod method. The method appears to be accurate and can be used to follow adhesion tension changes, and hence gives information concerning free surface energy changes which occur on the surface of solids. The solids studied in this investigation were Pyrex, silica, gold, and platinum.

2. It has been shown that the precise method of pretreatment of a solid surface is important in a study of its surface properties.

3. The presence of strains in glass appears to account for the large water-air contact angles observed on strained glass surfaces. Removal of the strain by careful annealing decreases the contact angle of water on such surfaces to zero.

4. Aging of glass and metal surfaces increases the magnitude of the solid-liquid-air contact angle formed upon them.

5. Heat treatment of solids can greatly alter the magnitude of the contact angle.

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